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Canada Centre for Mineral and Energy Technology
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ON-LINE DATA COLLECTION, MASS TRANSFER COEFFICIENTS, AND PRELIMINARY PREAERATION RESULTS IN A BENCH SCALE REACTOR

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Modelling and Process Control in Gold Cyanidation

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On-line Data Collection, Mass Transfer Coefficients, and Preliminary Preaeration Results in a Bench Scale Reactor

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Abstract

A small bench scale reactor was equipped with several probes and instruments that allowed on-line monitoring of pH, dissolved oxygen concentration, and temperature. The probes were connected to a computer through a μMAC-6000 data acquisition and control board. The collected dissolved oxygen concentration data were used to estimate gas/liquid mass transfer coefficients in the reactor using an appropriate mass transfer model.

A series of preliminary tests on the effect of preaeration of gold ores has been completed. Results have shown that preaeration of a gold ore will significantly reduce the quantity of cyanide consumed during the cyanidation step. Results in which pure oxygen was used were encouraging since a greater proportion of cyanide was complexing with gold and silver and less cyanide was complexing with impurities

such as iron and copper compared to samples that were not preaerated or preaerated with air.

This report is the first in the experimental work of the project on modelling and process control in gold cyanidation and outlines attempts to automate the reactor, measure and optimize oxygen transfer, and study the effect of oxygen in gold processing. Many improvements are still needed and several of the results are inconclusive.

Keywords: gas/liquid mass transfer, on-line data acquistion, gold ore preaeration, gold ore cyanidation

Résumé

Un petit réacteur expérimental a été équipé de plusieurs sondes et instruments permettent le contrôle en circuit du pH, de la concentration d'oxygène dissous et de la température. Les sondes ont été reliées à un ordinateur par un panneau de saisie des données et de commande μMAC-6000. Les données recueillies sur la concentration d'oxygène dissous ont servi à estimer les coefficients de tranfert de masse gaz/liquide dans le réacteur selon un modèle approprié de transfert de masse.

Une série d'essais préliminaires sur l'effet de la préaération des minerais d'or a été réalisée. Les résultats ont révélé que la préaération

d'un minerai d'or réduit sensiblement la consommation de cyanure pendant la cyanuration. Les résultats avec de l'oxygne pur ont été encourageants à cause de la meilleure complexation du cyanure avec l'or et l'argent qu'avec des impuretés comme le fer et le cuivre par rapport aux échantillons non préaérés ou préaérés avec de l'air.

Le présent rapport est le premier des travaux expérimentaux du projet sur la modélisation et la régulation des procédés de cyanuration de l'or, et il décrit les efforts tentés pour automatiser le réacteur, mesurer et optimiser le transfert d'oxygène, et étudier l'effet de l'oxygène dans le traitement de l'or. Il resterait à apporter de nombreuses améliorations, tandis que plusieurs résultats ne sont pas concluants.

Mot-clés: transfert de masse gaz/liquide, préaération des minerais d'or, cyanuration d'or, compilation en continu de données

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1 Introduction

Leaching processes often require oxygen as an oxidant. The source of oxygen is usually air although in some applications, particularly pressure leaching and gold cyanidation, pure oxygen is either used or is being considered.

Leaching with oxygen as a reactant is an example of a three phase reaction system. The presence of three phases offers a challenge in modelling and operation. Typically, the reaction modelling of the process requires consideration of a number of factors [1]:

- transport of gas through the gas/liquid interface;
- transport of reactants through the solid/liquid interface;
- adsorption of reactants at an active site on the solid;
- chemical reaction on the solid surface;
- desorption of products from the surface;
- transport of the products from the solid back to the bulk liquid.

One or a combination of these steps will characterize the system by being the rate limiting step. In leaching systems, the adsorption and desorption steps are usually assumed to be rapid and therefore not rate limiting. In gold cyanidation, evidence has suggested that the dissolution reaction on the surface is rapid as well. Habashi [2] carried out an analysis based on the assumption that the rate limiting step is the transport of reactants from the

bulk liquid to the gold surface through an interface or boundary layer. The resultant equation describing the phenomenom is:

$$Rate = \frac{2A\mathcal{D}_{CN^-}\mathcal{D}_{O_2}[CN^-][O_2]}{\delta\{\mathcal{D}_{CN^-}[CN^-] + 4\mathcal{D}_{O_2}[O_2]\}} \quad (1)$$

where A = surface area of gold

$\mathcal{D}_{CN^-}, \mathcal{D}_{O_2}$ = diffusivities of CN^- and O_2

$[CN^-], [O_2]$ = concentrations of CN^- and O_2

δ = thickness of Nernst boundary layer.

Other research has shown that the rate of dissolution of gold is highly dependent on the concentration of dissolved oxygen [3]. Dissolved oxygen concentration frequently depends on the gas/liquid mass transfer rate. The gas/liquid and liquid/solid mass transfer rates can therefore be expected to be significant steps in the process.

Many of the side reactions that occur in the processing of gold ores require oxygen as well [4]. Evidence suggests that the rates of these oxidation reactions are dependent on the dissolved oxygen concentration. It is expected that the preaeration reactions would proceed more rapidly under conditions of high oxygen concentration.

In order to develop a better understanding of preaeration and gold cyanidation, a small bench scale reactor has been devised. Initially, experiments were carried out to determine the conditions for optimum gas/liquid mass transfer rates in the reactor. The effect of gas flow rate, liquid pumping rate, and solids content of the slurry on the mass transfer coefficient were evaluated. Silica sand, ground to a size fraction similar to that of a gold ore used in

subsequent preaeration tests was used. A central composite experimental design was implemented to account for any curvature in the response (i.e., data not well represented by a straight line). The data of the experimental design were used to determine an optimum set of operating conditions for the use of the reactor as a gold ore preaerator where both air and oxygen were used.

2 Theory

2.1 Gas/Liquid Mass Transfer

Gas/liquid contacting and transfer are important components of many mineral and chemical processes. Their application is varied and includes such operations as distillation, gas absorption in air pollution control, and gas introduction to heterogeneous reaction systems such as those encountered in leaching operations. This third example is the focus of the present investigation.

The extraction of gold from its ores requires a large amount of oxygen, principally to oxidize gold during cyanidation, but it is also consumed as a reactant in the many side reactions that accompany gold extraction. Oxygen is supplied to the process from the gaseous state as either pure oxygen or air. An efficient gas contacting operation is required to provide sufficient quantities of oxygen to the process.

Gas/liquid mass transfer is expressed through the following equation [5]:

$$\frac{dC}{dt} = k_L a \left(C_\infty - C\right) \tag{2}$$

where C = concentration of solute in the solvent

k_L = liquid side mass transfer coefficient

a = specific interfacial area

C_∞ = solubility of the solute in the solvent.

Equation 2 can be integrated from initial time, $t = 0$, and solute concentration, $C = C_o$, to time, $t = t$, and concentration, $C = C$, to yield:

$$C = C_\infty - (C_\infty - C_o) \exp(-k_L a t) \tag{3}$$

It is therefore possible to evaluate the term, $k_L a$, by fitting transient oxygen concentration data using nonlinear regression.

The type of mass transfer equipment, the physical properties, and the operating conditions are all important aspects in determining the value of $k_L a$. The objective in equipment design and operation is often maximizing this quantity since the larger it is, the higher the rate of mass transfer becomes. Once a system has been specified and the equipment chosen, it is necessary to have a process to determine the best conditions under which to operate the system. An examination of the literature of gas/liquid mass transfer equipment suggested that the mass transfer coefficient is a function of gas flow rate, slurry pumping rate, and the solids content [5, 6, 7, 8]. Temperature is also an important variable but the experiments in this study were carried out at ambient conditions. Temperature control was not considered.

2.2 Central Composite Design

The central composite design is an experimental design specifically devised to handle situations in which curvature in the response surface is expected [9]. If the curvature corresponds to a peak, then it should be possible to locate optimum values for the operating variables. In the present case, the optimum values of gas flow rate, slurry flow, and solids content for maximum mass transfer rate will be determined.

The principle behind experimental design methodology is to identify major effects in a system by empirically fitting response data to a simple equation. In factorial and related designs, linear equations are used to represent the data, therefore, linear regression can be applied. The response data of a central composite design are fitted to a quadratic equation:

$$y = \beta_0 + \sum_{i=1}^{v} \beta_i x_i + \sum_{i=1}^{v} \beta_{ii} x_i^2 + \sum_{i=1}^{v-1} \sum_{j=i+1}^{v} \beta_{ij} x_i x_j + \epsilon \qquad (4)$$

where y = dependent or response variable

x_i = independent or operating variables

v = total number of operating variables

$\beta_0, \beta_i, \beta_{ii}, \beta_{ij}$ = regression coefficients

ϵ = random error.

In this investigation the three operating variables that were considered were the gas flow rate, slurry flow or recirculation rate, and solid content of the slurry. The primary dependent or response variable of interest was $k_L a$, the product of mass transfer coefficient and specific interfacial area from

Equation 3. The solubility, C_∞, was also examined as a dependent variable. The central composite design provided the level of the operating variables to be used for each of the experimental runs. These levels were specified so that the maximum amount of information could be gathered in the fewest number of runs. The levels of the operating variables for this study have been given in Table 1.

The operating data entered into a regression routine are often scaled so that all of the operating or independent variables are of the same order of magnitude and comparison of variable effects can be made. In central composite designs the following transformation to the independent variables is used:

$$X_i = \frac{(x_i - \bar{x}_i)}{\frac{1}{2} \text{ the range of } x_i} \tag{5}$$

where X_i = coded value of variable, i

x_i = real value of variable, i

$\bar{x}_i$ = mean of variable, i

It should be noted that range used in these coding calculations is based on data associated with the 2 level factorial design inherent in the experimental plan. The coding does not include the so-called axial points of the design. In this case, the values of operating variables for Runs 13-16 of Table 1 were not used to calculate the range. A more detailed description of the coding procedure and its significance may be found elsewhere [9]. The results of applying the transformation to each of the experimental runs has been given in Table 2.

Table 1: Operating Conditions According to the Central Composite Design

Run No.	Gas Flow Rate (L/min)	Slurry Flow Rate (L/min)	Solids Content (g)
1	0.30	1.000	100
2	0.30	1.400	150
3	0.50	1.000	150
4	0.50	1.400	100
5	0.40	1.200	125
6	0.40	1.200	125
7	0.30	1.000	150
8	0.30	1.400	100
9	0.50	1.000	100
10	0.50	1.400	150
11	0.40	1.200	125
12	0.50	1.200	125
13	0.57	1.200	125
14	0.23	1.200	125
15	0.40	1.536	125
16	0.40	0.864	125
17	0.40	1.200	167
18	0.40	1.200	83
19	0.40	1.200	125
20	0.40	1.200	125

Table 2: Operating Conditions in Coded Form

Run No.	Gas Flow Rate	Slurry Flow Rate	Solids Content
1	-1.00	-1.00	-1.00
2	-1.00	1.00	1.00
3	1.00	-1.00	1.00
4	1.00	1.00	-1.00
5	0.00	0.00	0.00
6	0.00	0.00	0.00
7	-1.00	-1.00	1.00
8	-1.00	1.00	-1.00
9	1.00	-1.00	-1.00
10	1.00	1.00	1.00
11	0.00	0.00	0.00
12	0.00	0.00	0.00
13	1.70	0.00	0.00
14	-1.70	0.00	0.00
15	0.00	1.68	0.00
16	0.00	-1.68	0.00
17	0.00	0.00	1.68
18	0.00	0.00	-1.68
19	0.00	0.00	0.00
20	0.00	0.00	0.00

A multiple linear regression routine was used to estimate the values of the regression coefficients using the coded values of the independent variables. The magnitudes of the regression coefficients determined whether the effect of a variable or combination of variables on the response was statistically significant. Examination of the regression coefficients, therefore, indicated which variables described the behaviour of k_La or C_∞. The model given in Equation 4 was thereby reduced to a simpler equation by the elimination of statistically insignificant terms. In this investigation, the process was automated by employing a stepwise regression procedure provided in STATGRAPHICS, a commercially available statistical software package [10].

3 Experimental

3.1 Experimental Apparatus

A glass reactor was developed for carrying out bench scale aeration experiments. It consisted of a cylindrical section with an outside diameter of 64 mm and a height of 95 mm. The conical bottom of the reactor was tapered to a diameter of 7 mm over a length of 75 mm giving an overall length to the reactor of 170 mm. Fittings were attached to the body of the reactor to accommodate a pH electrode, thermocouple, and a dissolved oxygen electrode. The gas contacting apparatus consisted of an annular tube. The shell was a glass cylinder with an outside diameter of 28 mm and a length of 200 mm. The inner tube was made of porous plastic, 190 mm long, with an outside diameter of 12 mm and a thickness of 9 mm.

The two pieces of equipment were connected with rubber tubing. The connections were made so that slurry flowed through the inner tube. Gas flowed into the shell of the annulus then travelled through the tube pores into the slurry. The slurry and entrained gas then returned to the main body of the reactor (Figure 1).

A Masterflex pump with a flow rate range of 0 to 1600 mL/min was used to pump the slurry and a Matheson Model 8200 mass flow controller was used to regulate the flow of compressed air, oxygen or nitrogen to the system. The slurry was pumped from the bottom of the reactor to the top of the gas contacting section. After air or oxygen was entrained in the slurry it returned to the main body of the reactor through an entrance located on the side near the middle of the reactor.

The temperature, pH, and dissolved oxygen were continuously measured and recorded to a file in a computer. Temperature was measured with a Type K thermocouple while a Radiometer type GK2401/C pH electrode was used to measure pH. Dissolved oxygen was measured with an Orion Model 97-08-00 dissolved oxygen electrode capable of measuring dissolved oxygen in the range 0-14 ppm. This low range dictated that air be used in the mass transfer experiments since preliminary tests with oxygen indicated dissolved oxygen levels higher than 14 ppm. The thermocouple and pH electrode were inserted through the top of the reactor and the dissolved oxygen probe was inserted horizontally through the side of the reactor to abate fines accumulation on the membrane.

The devices were connected to the computer via an Analog Devices μMAC-6000 data acquisition board (Figure 2). The thermocouple and the dissolved

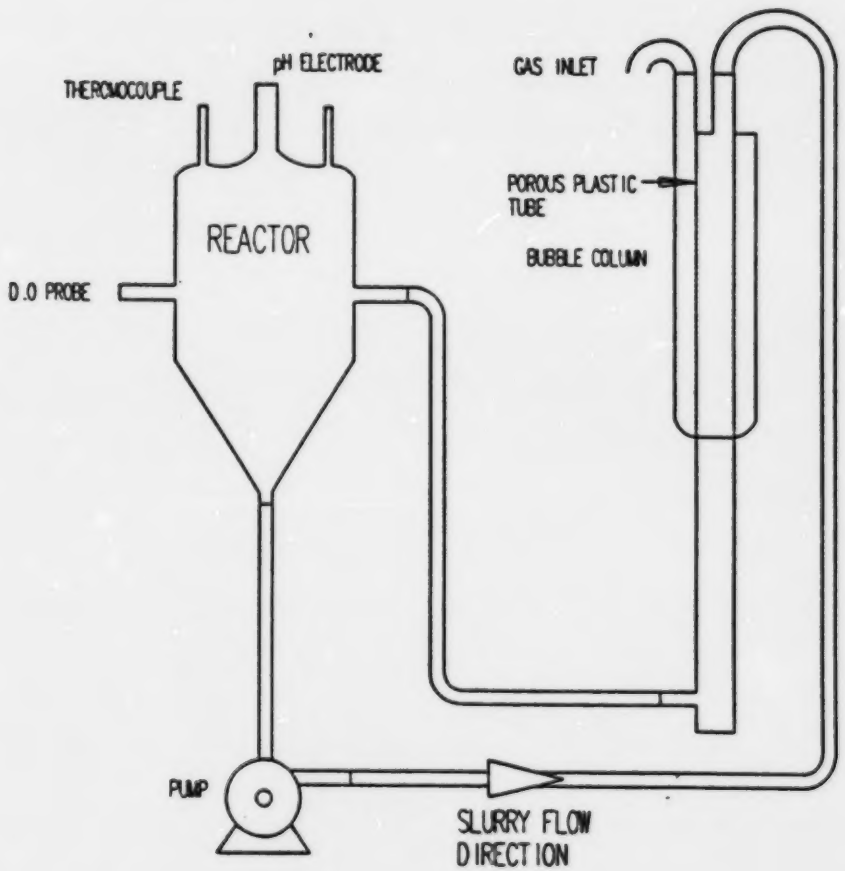

Figure 1: Diagram of Apparatus including Main Body and Gas/liquid Contactor

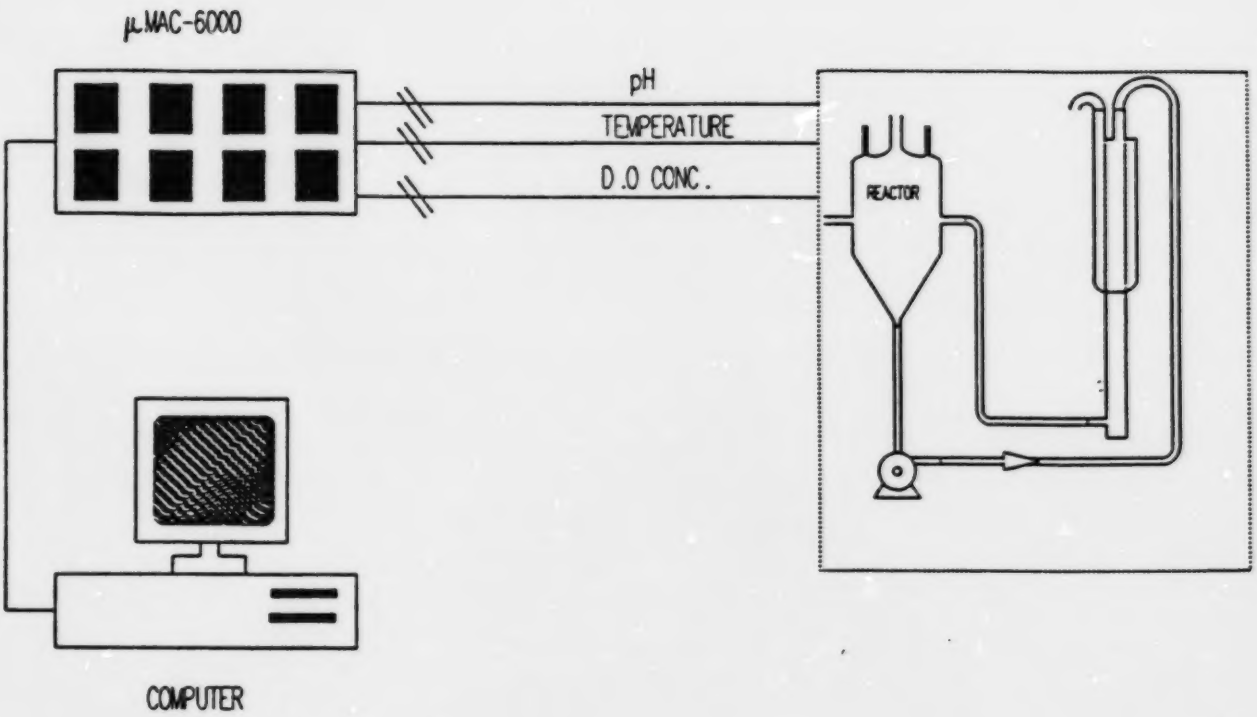

Figure 2: Layout of Equipmment including the μMAC-6000 and Computer

oxygen electrode were connected directly to appropriate modules mounted on the data acquisition board. The thermocouple was connected to an Analog Devices type 5B37-K-02 module specifically designed for reading type K thermocouple signals. The dissolved oxygen electrode was connected to a type 5B31-01 module that read a ± 1V signal delivered by the electrode. The voltage signal was calibrated and translated into ppm through an internal program in the μMAC-6000. The calibration equation was determined by linear regression to be:

$$C = -16.9V + 7.0 \tag{6}$$

where C = dissolved oxygen concentration, ppm

V = voltage delivered by D.O. probe, volts.

This calibration equation is the same as that reported by Argyropoulos and Chen [11] for a similar probe.

Because of the high impedance across the glass electrode of the pH probe, it could not be directly connected to a μMAC-6000 module. One option was to use a preamplified pH electrode, however, the electrode of this type that was available was too large to fit on the reactor. Instead, a standard pH electrode was connected to a Radiometer Ion 85 ion analyzer. Leads from the recorder outlet of this meter were then connected to an Analog Devices type 5B31-02 module on the acquisition board.

Employing the pH meter was beneficial since the literature provided with the meter described in detail the way in which the voltage and temperature signals delivered by the electrode and a thermocouple were used to calculate

and indicate the pH with automatic temperature compensation [12]. A three point calibration on the pH electrode was carried out daily. This calibration procedure consisted of taking measurements of pH of two known buffer solutions at room temperature and a third measurement was taken at a different temperature. With these readings the meter calculated the following constants:

1. pH_0, the 'zero' pH
2. S, the sensitivity
3. pH_{iso}, the isopotential pH.

These quantities were then used by the meter to calculate the pH [12]:

$$pH = pH_0 \frac{T_1}{T_{SMP}} - \frac{E_{SMP}}{R'ST_{SMP}} + pH_{iso}\left(1 - \frac{T_1}{T_{SMP}}\right) \tag{7}$$

where T_1 = temperature of first calibration buffer, K

T_{SMP} = temperature of sample, K

E_{SMP} = voltage signal of the electrode, V

$R' = \frac{R \ln 10}{zF}$

R = gas constant = 8.3143 J/(K·mol)

F = Faraday's constant = 96489 Coulombs

z = ion valence = 1 for hydrogen.

The constants evaluated for pH calculation were accessible to the operator by reading the memory stack of the meter. Equation 7 was installed into

the μMAC-6000 program along with the established constants. In this way, the thermocouple attached to the μMAC-6000 and the analog voltage signal delivered from the meter to the μMAC-6000 were used to convert this voltage to pH. Periodic comparisons of the pH calculated in the μMAC-6000 with the reading from the meter indicated that the use of Equation 7 was valid.

3.2 Experimental Procedure in Aeration Studies

A volume of 300 mL of distilled water was added to the reactor and the pump was started to begin the circulation. Silica sand of -200 mesh was added through the top of the reactor and nitrogen was introduced to the slurry to purge it of dissolved oxygen. Once the dissolved oxygen, as measured through the D.O. probe, had reached a value close to 0, air was introduced at the desired flow rate. A period of 20-30 seconds was allowed to pass before turning on the computer to wait for the gas lines to be cleared of nitrogen. Data were collected until the dissolved oxygen reached a steady value.

3.3 Preaeration of a Belmoral Concentrate

The experimental procedure of the previous section was used to define optimum conditions for the aeration of a Belmoral concentrate. Based on the results of the central composite design, the gas flow rate for all tests was set at 0.6 L/min. Slurry pumping rate and solid content were set at 1.2 L/min and 110 g, respectively while the liquid volume was 300 mL.

The preaeration experiments were carried out in a basic solution consisting of water and lime. The target pH for each of the experiments was

11. During experimentation, the pH tended to drop due to the acidic nature of the ore, to chemical reactions, or to the formation of carbonic acid from absorbed CO_2.

Flotation reagents created foaming in early runs that resulted in an overflow in the reactor. This problem was remedied by forming a pulp and stirring the concentrate with methanol for an hour to remove the flotation reagents.

The following procedure was used for all runs:

1. The solution was adjusted to a pH of approximately 11.
2. The solids were added to the reactor as quickly as possible.
3. Either air or oxygen was sparged through the aerator at the prescribed flow rate of 0.6 L/min.
4. Dissolved oxygen, pH, and temperature were recorded on the computer over the length of the experiment.
5. After the prescribed aeration time of 2, 4, or 6 hours, the slurry was filtered and washed. A sample of filtrate was saved for SO_4^{2-} analysis[1].
6. The solid residue was weighed to determine any weight loss.

3.4 Cyanidation of Preaerated Samples

The cyanidation of the preaerated concentrate was carried out in a 400 mL beaker at a stirring speed of 600 rpm. A 100 g sample from the preaeration

[1]The possibility that some of the SO_4^{2-} precipitated as $CaSO_4$ was not considered but will be considered in future experiments.

experiment was added to a fresh solution consisting of water and lime to yield a slurry concentration of 33% solids. Cyanide (as 0.5 g of NaCN) was added to the solution at the beginning of a run except in the 24 hour tests, when it was added in two stages: half of the cyanide in the beginning, the second half 6 hours later. The cyanidation times varied between 3 and 24 hours. The pH was adjusted to remain close to 11 through the addition of CaO at intervals throughout the cyanidation. Total addition of CaO was noted. Oxygen was supplied to the slurry by means of any dissolved oxygen initially present in the solution and through surface aeration.

All of the experiments were compared against a 24-hour cyanidation test that was carried out without preaeration. It was known that the gold in the Belmoral concentrate was amenable to conventional cyanidation and it was therefore assumed that improvements through preaeration might appear through comparable extractions being observed for much shorter extraction times. A reduction in cyanide consumption was also considered to be an improvement. Another blank test was carried out that included withdrawal of samples so that a transient profile of gold extraction could be developed. Problems in the sampling procedure precluded any meaningful results being obtained, although the results of this experiment are presented.

Two samples of the ore were preaerated with air for two hours and then subjected to a 24 hour cyanidation. The first test was carried out without withdrawal of samples while the second test involved some sampling where mass and volume correction problems were experienced. All of the cyanidation experiments, to this point, had a small quantity of $Pb(NO_3)_2$ added to alleviate problems associated with soluble sulphide compounds. An oversight

in the procedure after this time resulted in the absence of $Pb(NO_3)_2$ in all subsequent experiments.

A series of preaeration tests with air was carried out using a 2 level factorial design as a basis. The operating variables for this investigation were the preaeration and cyanidation times at two different values for each respective time. Similar runs using pure oxygen were also performed. A summary of these experimental runs is given in Table 3. It should be noted that only the first 4 runs were carried out with $Pb(NO_3)_2$ added to the cyanide solution (Tests #1 and 2, Blanks #1 and 2). The remaining runs were carried out without $Pb(NO_3)_2$, the absence of which was considered to be one of the causes of minor discrepencies that appeared in the results.

3.5 Chemical Analysis of Solutions and Solids

The preaeration solutions were analyzed for sulphate while the pregnant solutions, after cyanidation, were analyzed for gold, silver, copper, and free cyanide. Atomic absorption spectrophotometry was used to test the pregnant solution for the metals. Extractions based on the concentration of gold and silver in solution were later verified with analyses of the solid residues performed by the Chemical Laboratories of MSL.

Sulphate content of the preaeration solution was determined by mixing a 25 mL aliquot of solution with an excess of $BaCl_2$ solution [13]. Upon addition of the $BaCl_2$, a white precipitate of $BaSO_4$ was formed that was filtered, dried, and weighed. The quantity of SO_4^{2-} initially in the preaeration solution was then determined gravimetrically.

Table 3: Experiments of Belmoral Concentrate at Various Preaeration and Cyanidation Times

Test No.	Preaeration Time (hrs)	Cyanidation Time (hrs)
Blank #1	-	24
Test #1	2	24
Blank #2	-	24
Test #2	2	24
BC-PRE4-3	4	3
BC-PRE6-3	6	3
BC-PRE6-6	6	6
BC-PRE4-6	4	6
BC-PRE4-3A	4	3
BC-OX4-3	4	3
BC-OX6-3	6	3
BC-OX4-6	4	6
BC-OX6-6	6	6

Free cyanide in the pregnant solution was determined by titrating a sample with a solution of $AgNO_3$ of known concentration using Rhodanine as the indicator. The natural yellowish colour of the pregnant solution mildly interfered with the observation of the end point and may have accounted for some precision error in the determinations.

4 Results and Discussion

4.1 Aeration Tests

The data from the experimental runs were collected in a Compaq XT compatible computer. The computer files for each experiment were put into a form that was readable by the STATGRAPHICS statistical software. The data were generally quite smooth and had a well defined profile. Examples of the dissolved oxygen-time profiles have been given in Figures 3 and 4. The dissolved oxygen and time were then used to fit the data to Equation 3 using the nonlinear regression routine provided with STATGRAPHICS. Initially, three parameters were fitted to the data:

1. C_0
2. k_La
3. C_∞.

The nonlinear regression often fitted the data so that C_0 was less than 0 which was physically impossible. Alternatively, Equation 3 was forced through the first data point (i.e., C_0 set at C_1 where C_1 was first data point).

As seen in the results given in Table 4, this had little effect on the fitted values for k_La and C_∞.

Linear regression was applied to the values of k_La and C_∞ estimated by the two parameter fit of Equation 3 as dependent variables and the values of the gas and slurry flow rates and solids concentration as independent variables.

The data were fitted to the linear equation, Equation 4. Fitting the data for k_La to Equation 4 yielded the following reduced equation after the removal of statistically insignificant terms:

$$k_La = 0.0165 + 0.0033Q - 0.0012Q^2 - 0.0016LS \qquad (8)$$

where Q = coded gas flow rate

L = coded slurry flow rate

S = coded solid content.

The equation, particularly with respect to the gas flow rate, was in good agreement with theory. Most correlations for gas/liquid mass transfer operations have indicated that mass transfer rates should increase with increasing gas flow rate. The presence of the quadratic term for gas flow rate and its sign suggested that this increase would not be unbounded. Intuitively, it was suspected that the true behaviour of mass transfer rate would tend asymptotically towards a maximum with increasing gas flow rate. This was verified by carrying out further tests in which the gas flow rate was increased beyond the optimum value prescribed by Equation 8.

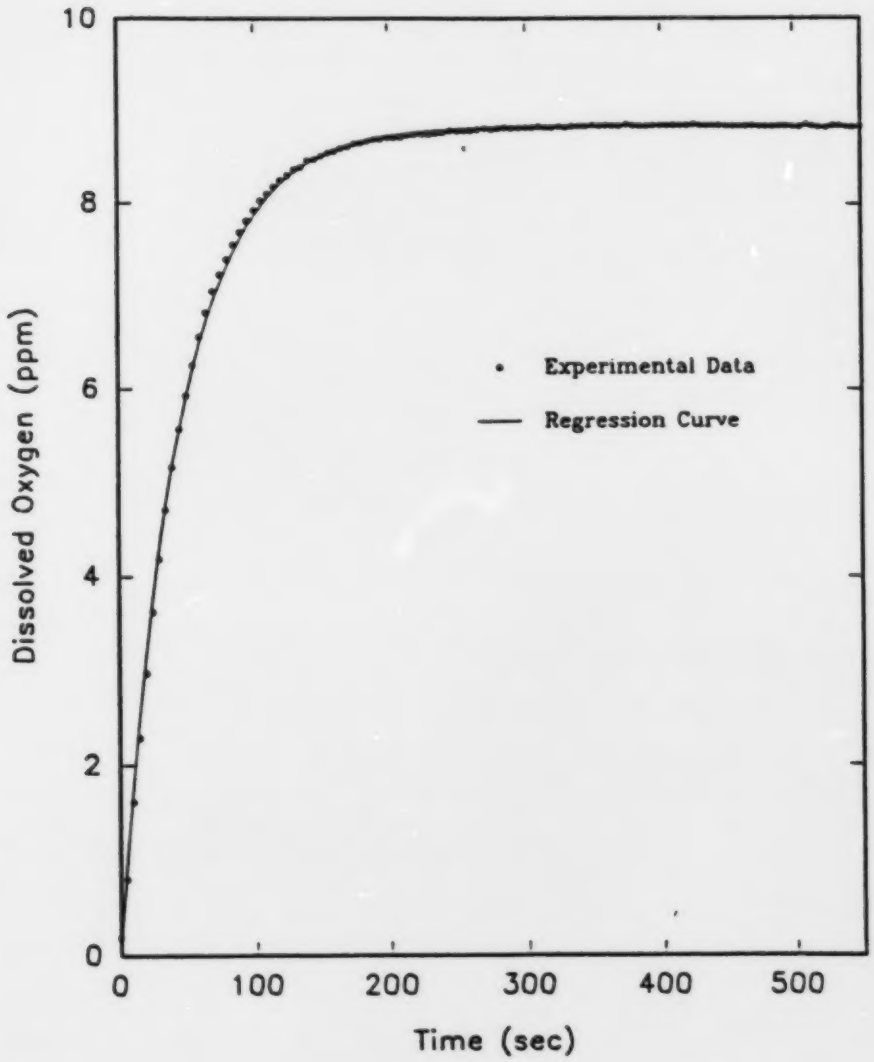

Figure 3: Oxygen Concentration in Solution as a Function of Time for Run 4 from Table 4 (Gas flow rate = 0.5 l/min, Slurry flow rate = 1.4 l/min, Solids content = 100 g)

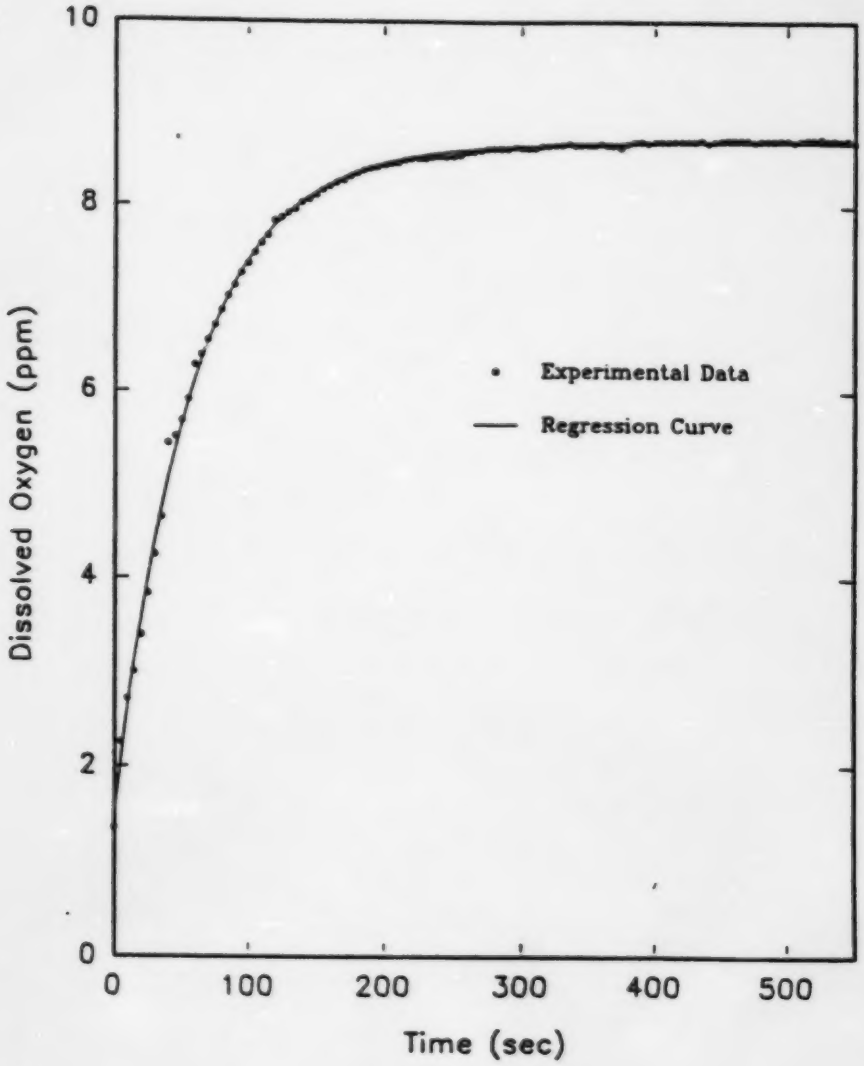

Figure 4: Oxygen Concentration in Solution as a Function of Time for Run 20 from Table 4 (Gas flow rate = 0.4 l/min, Slurry flow rate = 1.2 l/min, Solids content = 125 g)

Table 4: Results of Aeration Study: Values of k_La, C_∞, and C_o Evaluated by Nonlinear Least Squares

Three Parameter Fit				Two Parameter Fit	
Run No.	k_La	C_∞	C_0	k_La	C_∞
1	0.0148	8.773	0.681	0.0145	8.779
2	0.0066	8.707	-0.031	0.0063	8.729
3	0.0208	8.692	0.068	0.0205	8.694
4	0.0225	8.826	-0.119	0.0217	8.830
5	0.0173	8.680	1.458	0.0176	8.676
6	0.0175	9.149	-0.003	0.0167	9.151
7	0.0129	8.613	-0.082	0.0123	8.622
8	0.0140	8.858	-0.294	0.0132	8.867
9	0.0180	8.668	-0.013	0.0175	8.672
10	0.0176	8.792	-0.406	0.0164	8.808
11	0.0173	8.680	1.470	0.0177	8.676
12	0.0179	8.485	-0.039	0.0172	8.495
13	0.0173	8.836	1.793	0.0173	8.836
14	0.0090	8.665	-0.117	0.0084	8.691
15	0.0141	8.736	0.703	0.0136	8.744
16	0.0159	8.410	0.353	0.0157	8.413
17	0.0180	8.580	0.959	0.0180	8.580
18	0.0193	8.788	0.862	0.0192	8.787
19	0.0142	8.634	1.170	0.0145	8.627
20	0.0148	8.602	-0.029	0.0140	8.619

The optimum value was determined at the center point values of liquid pumping rate and solid content ($L = S = 0$). According to Equation 8, this optimum should occur at a gas flow rate of 0.534 L/min yielding a value of k_La of 0.0188 s^{-1}. This value was comparable to that obtained experimentally at a gas flow rate of 0.57 L/min where a value of k_La of 0.0173 s^{-1} was observed. Further tests were conducted at gas flow rates of 0.55 and 0.72 L/min. These tests yielded results for k_La of 0.0264 and 0.0254 s^{-1}, respectively suggesting that within the limits of experimental error that a maximum value of approximately 0.026 s^{-1} could be expected between the aforementioned flow rates. It was concluded that increasing the gas flow rate beyond 0.72 L/min would not increase the mass transfer coefficient and the presence of a maximum value was confirmed. Subsequent aeration experiments involving Belmoral concentrate were therefore carried out at 0.6 L/min which was within the range of flow rates tested that yielded the maximum mass transfer coefficient.

Regression analysis of the oxygen solubility, C_∞, as a function of the operating variables revealed that none of the variables had an effect on C_∞. In other words, the values obtained and given in Table 4 were random. It was likely that, consistent with the theory describing gas solubility, that the values reflected variations in temperature and pressure.

Temperature differences were also suspected of playing a role in the rather wide scattering of mass transfer coefficient results. Other contributing factors included possible interference of oxygen probe membrane performance by fines as well as wear and tear on the membrane due to the abrasive action of the slurry. The effect of these factors was not investigated.

The dynamic response of membrane type dissolved oxygen probes is often considered as a source of error in investigations of this type. The error occurs when the dynamic response of the probe is slow due to slow diffusion through the membrane. Measurements and calculations in this case tend to reflect the dynamics of the probe rather than the dynamics of the mass transfer in the aerating system. In particular, this phenomenon results in inaccurate mass transfer coefficient estimates. If the dynamic response of the probe is sufficiently rapid, the mass transfer coefficients evaluated earlier should be accurate.

The dynamic response of the dissolved oxygen probe used in this study was evaluated by immersing the probe in an oxygen saturated solution followed by immersion in a sodium sulphite solution containing cobalt. The second solution was known to be devoid of oxygen because of the cobalt catalyzed reaction [14, 15, 16]:

$$O_2 + 2Na_2SO_3 \xrightarrow{CoSO_4} 2Na_2SO_4 \tag{9}$$

The response of the probe to this step change in oxygen concentration was measured and the data were fitted to an exponential decay to yield the following (see Figure 5):

$$C = 8.112 \exp(-0.097t) \tag{10}$$

A measure of the response of the probe is given by the time constant, 0.097. This value was compared to the values of the mass transfer coefficient given in Table 4. The time constant was approximately 5 to 6 times greater than the mass transfer coefficients. More work should be carried out to determine

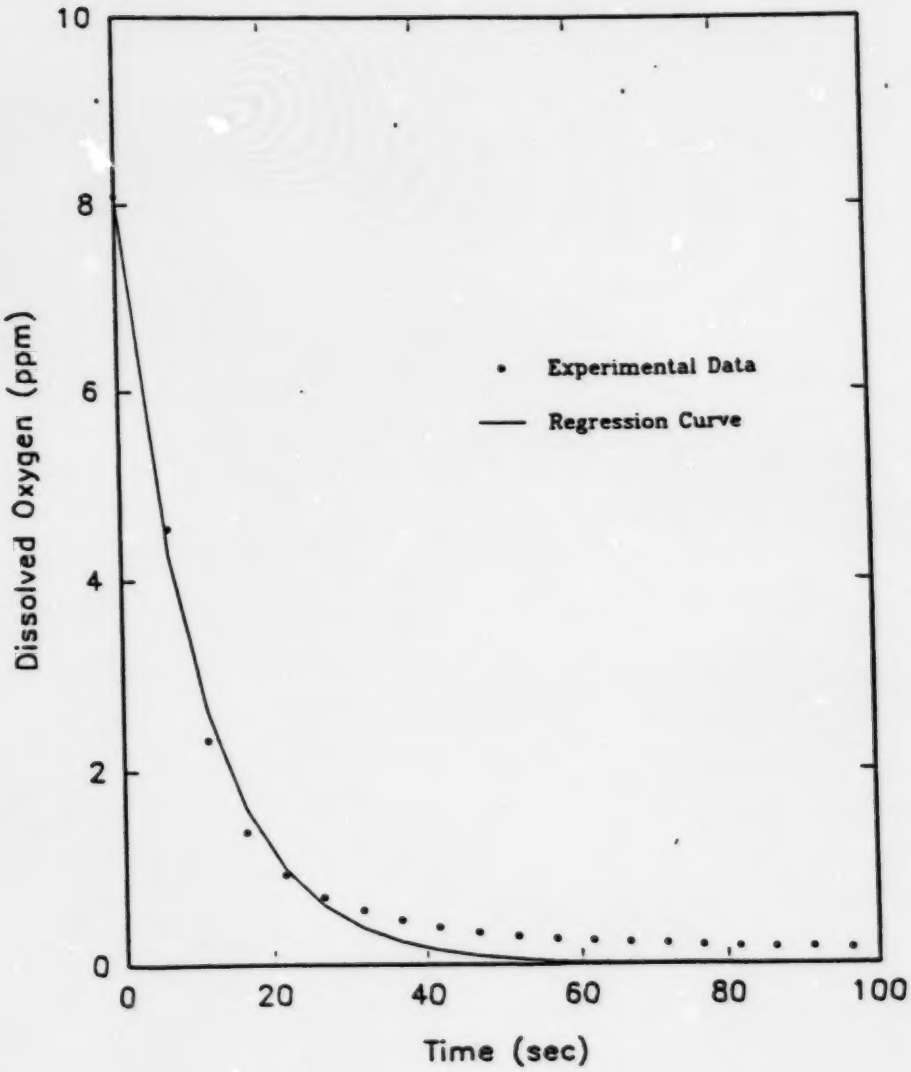

Figure 5: The Dynamic Response of the Oxygen Probe

whether this is large enough so that the probe dynamics are not significantly affecting the measured values of $k_L a$.

4.2 Belmoral Concentrate Preaeration Results

Preaeration of the concentrate yielded the results given in Table 5. There was a clear discrepency between the gold extractions determined through the analysis of the solutions and those of the solids. The solid analyses were deemed to be the more accurate results since they would not be subject to solution losses and dilution errors.

As may be seen in Table 5, the extractions for the first 4 runs were greater than those of the others. The main differences between these runs and the others were that $Pb(NO_3)_2$ was added to the first 4 runs and the cyanidation times were longer. Both of these facts would explain the higher extractions observed in these runs. The lack of $Pb(NO_3)_2$ in the solutions was an error that will be corrected in future experiments. The other fact that was clear from the results of the first 4 runs was that preaeration did not appear to have a beneficial effect on the extraction efficiency. All 4 runs yielded extractions of gold greater than 95%. However, the first 2 results, Blank #1 and Test #1 indicated a marked difference in the amount of consumed cyanide. The preaerated sample consumed considerably less cyanide than the untreated sample. The next 2 results contradicted this finding. In the case of Blank #2 and Test #2, the preaerated sample had a higher cyanide consumption. The reason for the apparent contradiction was traced to a change in procedure. Samples were periodically withdrawn from these tests in an attempt to

Table 5: Comparison of Extractions based on Solution and Solid Analyses for the Aeration Experiments of the Belmoral Concentrate: Gas Flow Rate = 0.6 L/min, Slurry Recirculation Rate = 1.2 L/min

Run No.	Extraction (Solution Analyses)			Extraction (Solid Analyses)	
	Au (%)	Ag (%)	Total Cu (mg)	Au (%)	Ag (%)
Blank #1	88.89	72.85	51.2	96.02	75.52
Test #1	82.43	75.11	50.2	95.77	78.64
Blank #2	85.53	90.50	50.7	95.18	81.04
Test #2	62.05	67.87	71.7	96.23	80.81
BC-PRE4-3	82.18	54.30	32.0	76.51	63.35
BC-PRE4-3B	73.79	63.35	34.5	68.49	62.49
BC-PRE6-3	84.70	54.30	35.8	77.29	63.44
BC-PRE6-6	91.40	63.35	37.0	89.58	72.31
BC-PRE4-6	93.08	63.35	36.0	92.27	72.90
BC-OX4-3	86.37	58.82	34.2	86.83	70.36
BC-OX6-3	72.12	58.82	34.0	75.91	62.44
BC-OX4-6	84.00	91.00	38.6	89.40	70.00
BC-OX6-6	79.00	86.90	39.4	88.50	71.40

develop a profile of the evolution of SO_4^{2-} in solution.The sample removal created problems in mass and volume corrections that precluded the completion of this particular analysis.

The next series of runs (BC-PRE4-3 to BCPRE4-6 in Table 6) were carried out to examine the effect that preaeration time and cyanidation time had upon cyanide consumption and gold extraction using air during preaeration. It was clear that greater extractions occurred with longer cyanidation times. It was also clear that the increased extraction was accompanied by an increase in cyanide consumption. It was important to estimate the portion of the consumed cyanide that was complexed with the extracted gold and silver. This amount was estimated by assuming that both metals complexed with cyanide as $Me(CN)_2^-$. The proportion of cyanide associated with the precious metals was then evaluated based upon the total amount of consumed cyanide. As may be seen from the results given in Table 7, the amount of cyanide consumed by the gold and silver was quite small. Based on the analysis of the concentrate and the copper extractions reported in Table 5 it was assumed that the remainder of the cyanide was associated with copper and iron.

The series of runs denoted by BC-OX4-3 to BC-OX6-6 in Table 6 were carried out using pure oxygen in the preaeration stage. As may be seen, similar preaeration and cyanidation times were used for these experiments as were used for those experiments using air. It was worth noting that pure oxygen proved to be superior in the experiments in which 4 hours preaeration was folllowed by 3 hours of cyanidation when compared to similar conditions

Table 6: Extraction and Cyanide Consumption Results for the Aeration Experiments of the Belmoral Concentrate: Gas Flow Rate = 0.6 L/min, Slurry Recirculation Rate = 1.2 L/min

Run No.	Preaeration Time (hrs)	Cyanidation Time (hrs)	Cyanide Consumption (%)	Extraction (Solid Analyses)	
				Au (%)	Ag (%)
Blank #1	-	24	50.2	96.02	75.52
Test #1	2	24	37.4	95.77	78.64
Blank #2	-	24	42.6	95.18	81.04
Test #2	2	24	54.3	96.23	80.81
BC-PRE4-3	4	3	20.0	76.51	63.35
BC-PRE4-3A	4	3	21.5	68.49	62.49
BC-PRE6-3	6	3	27.2	77.29	63.44
BC-PRE6-6	6	6	38.9	89.58	72.31
BC-PRE4-6	4	6	37.4	92.27	72.90
BC-OX4-3	4	3	23.4	86.83	70.36
BC-OX6-3	6	3	21.5	75.91	62.44
BC-OX4-6	4	6	31.6	89.40	70.00
BC-OX6-6	6	6	30.4	88.50	71.40

Table 7: Summary of Cyanide Consumption Analysis

Run No.	Consumed Cyanide $\times 10^{-3}$ mol	Extracted Gold $\times 10^{-5}$ mol	Extracted Silver $\times 10^{-5}$ mol	Cyanide with Gold and Silver (%)
Blank #1	5.122	5.812	1.547	2.87
Test #1	3.816	5.797	1.611	3.88
Blank #2	4.346	5.760	1.660	3.41
Test #2	5.540	5.824	1.656	2.70
BC-PRE4-3	2.041	4.634	1.299	5.81
BC-PRE4-3A	2.194	4.145	1.280	4.95
BC-PRE6-3	2.775	4.679	1.301	4.31
BC-PRE6-6	3.969	5.426	1.482	3.48
BC-PRE4-6	3.816	5.589	1.494	3.71
BC-OX4-3	2.387	5.258	1.443	5.62
BC-OX6-3	2.194	4.596	1.279	5.36
BC-OX4-6	3.223	5.411	1.434	4.25
BC-OX6-6	3.101	5.332	1.428	4.36

using air.

Preaeration experiments indicated that a larger proportion of the consumed cyanide was associated with the precious metals when pretreatment was performed. The preaeration experiments with pure oxygen were especially encouraging in this respect. The portion of cyanide consumption going towards gold and silver extraction when oxygen was used in preaeration was consistently larger than when air was used under similar conditions. There was an apparent trade off, however, since longer preaeration times resulted in lower gold extractions. It is important to note that in all cases the cyanidation times were quite short and that the absence of $Pb(NO_3)_2$ allowed cyanide complexation with sulphur and potential passivation of gold surfaces. Addition of $Pb(NO_3)_2$ to all future experiments may alleviate these problems.

A typical plot of the transient dissolved oxygen content and temperature during a preaeration test has been presented in Figure 6. This figure indicates that, with the exception of an initial, abrupt drop in dissolved oxygen concentration, it remained steady throughout the experiment. Similarly, the temperature experienced an initial rise before remaining steady for the rest of the experiment. The combined behaviour of these two variables suggested that the dependence of oxygen solubility upon temperature was being reflected in this behaviour. The rise in temperature could be indicative of the presence of exothermic reactions such as the oxidation of sulphide minerals. The steady behaviour of oxygen concentration indicated that the aeration process was supplying sufficient oxygen to the preaeration reactions. Although more work is required, the results indicated that a more practical approach could be taken. The system, as operated, was running in a semi-

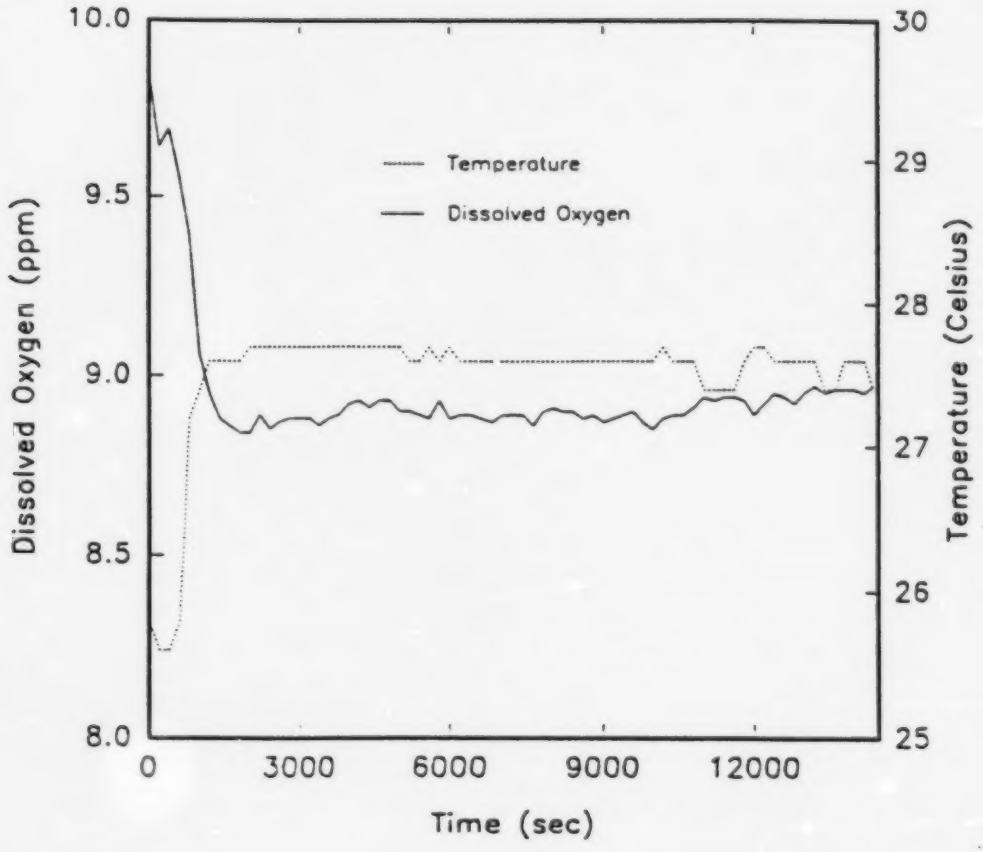

Figure 6: Typical Transient Dissolved Oxygen and Temperature Profiles during Preaeration of the Belmoral Concentrate

batch fashion since oxygen was continually added to a stable sample of ore. Therefore, once the solution became saturated with oxygen, the oxygen added afterwards was essentially wasted. A more practical approach would be to add oxygen until saturation after which oxygen addition could be stopped or reduced to maintain saturation. In this sense, the reactor would be a complete batch system. The transient dissolved oxygen profile would then give a measure of the extent of reaction for the various oxidation reactions occurring.

5 Conclusions and Recommendations

1. Interfacing of several instruments and probes to a computer through the μMAC-6000 data acquisition board was successful. Large amounts of data were easily collected and were amenable to analysis.

2. The aeration experiments demonstrated that the device used was typical of aeration systems in that the gas flow rate was the most important factor in determining mass transfer coefficients.

3. Less cyanide was consumed to obtain a given gold extraction when preaeration was performed.

4. Pure oxygen was beneficial to the preaeration of the ore. A larger proportion of cyanide was associated with gold and silver compared to no preaeration or preaeration with air.

5. Passivation of the gold surface by oxygen as well as lack of use of

$Pb(NO_3)_2$ was suspected of causing the observed lower extractions in the preaeration experiments. Longer cyanidation times might be required to achieve higher extrations, however, reasonable extractions occurred in as little as 6 hours.

Improvements to the experimental apparatus are being considered. These include the use of an oxygen probe capable of measuring higher concentrations, addition of pressure transducers, a constant temperature bath, oxidation-reduction potential probe, and a totalizer to determine the total amount of oxygen entering the reactor. It would also be beneficial to include instrumentation to determine the amount of oxygen exiting the reactor through the vent. In this way, an oxygen balance can be carried out to determine the amount of oxygen consumed during pretreatment.

The relatively slow response of the dissolved oxygen probe indicated that it might be prudent to use other methods for determining the mass transfer rate. The oxidation of sodium sulphite to sodium sulphate in the presence of a cobalt catalyst is frequently used for this purpose [14, 15, 16]. The disadvantage of using this chemical method is that the system cannot be implemented on-line. It would therefore be advisable to continue using the probe in conjunction with the chemical method and determine the magnitude of any adverse effects due to slow probe dynamics.

Data indicated that the dissolved oxygen concentration remained constant during preaeration. This suggested that the gas/liquid mass transfer rate was much greater than the consumption rate even when air was used. Therefore, sufficient oxygen was always available for the oxidation reactions

associated with pretreatment. With this in mind, it is recommended that future experiments follow a procedure in which the oxygen is charged to the system until saturation after which time the oxygen flow is stopped until dissolved oxygen levels drop to a critical level.

Pure oxygen has proven to be beneficial to the cyanidation process. Oxygen during the cyanidation tests carried out in this study was that already dissolved in solution and oxygen provided through surface aeration. Introducing pure oxygen in the cyanidation tests should be considered.

Several procedural aspects in studying oxygen use in gold processing were successfully resolved. A few remaining items still require resolution. These items will be examined in the next series of experiments in order to increase the chemical understanding and improve oxygen use in gold processing.

References

[1] J. M. Smith. *Chemical Engineering Kinetics.* McGraw-Hill, New York, 3rd edition, 1981.

[2] F. Habashi. *Principles of Extractive Metallurgy, Volume 2: Hydrometallurgy.* Gordon and Breach, New York, 1980.

[3] N. Hedley and H. Tabachnick. *Chemistry of Cyanidation.* Technical Report Mineral Dressing Notes No. 23, American Cyanamid Co., June 1958.

[4] I. A. Kakovskii and E. M. Kosikov. Study of the kinetics of oxidation of some sulphide minerals. *Obogasch. Rud.*, 20(3):18–21, 1975.

[5] R. E. Treybal. *Mass Transfer Operations.* Mcgraw-Hill, New York, 3rd edition, 1980.

[6] K. Shugerl. New bioreactors for aerobic processes. *Int. Chem. Engng*, 22(4):591–610, 1982.

[7] J. B. Joshi, A. B. Pandit, and M. M. Sharma. Mechanically agitated gas-liquid reactors. *Chem. Engng. Sci.*, 37(6):813–844, 1982.

[8] W.-H. Hong and H. Brauer. Gas-liquid mass transfer in bubble-column reactors. *Int. Chem. Engng*, 29(3):388–434, 1989.

[9] N. R. Draper and H. Smith. *Applied Regression Analysis.* John Wiley and Sons, 2nd edition, 1981.

[10] *STATGRAPHICS Statistical Graphics System User's Guide.* STSC Inc.

[11] S. A. Argyropoulos and T. C. M. Chen. *Development of Monitoring and Process Control Equipment for Use in Gold Cyanidation.* Technical Report, Dept. of Metallurgy and Materials Science, University of Toronto, May 1991. for Canada Centre for Mineral and Energy Technology, Energy, Mines, and Resources, Canada, DSS Contract No. 055SS.2344-9-9282.

[12] *Ion85 Ion Analyzer User's Handbook.* Radiometer Copenhagen.

[13] A. J. Vogel. *A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis.* Longman Group Ltd., London, 3rd edition, 1962.

[14] T. Reith and W. J. Beek. The oxidation of aqueous sodium sulphite solutions. *Chem. Engng. Sci.*, 28:1331–1339, 1973.

[15] M. Zaisha, Y. Shouzhi, and C.-Y. Chen. Preliminary studies on gas-liquid mass transfer in a gas-lift reactor. In K. Osseo-Asare and J. D. Miller, editors, *Hydrometallurgy Research, Development, and Plant Practice: Proceedings of the 3rd International Symposium on Hydrometallurgy*, pages 789–806, The Metallurgical Society of A.I.M.E., March 6-10 1983.

[16] G. Ruchti, I. J. Dunn, J. R. Bourne, and U. von Stockar. Practical guidelines for the determination of oxygen transfer coefficients ($K_L a$) with the sulfite oxidation method. *Chem. Engng. J.*, 30:29–38, 1985.

Government of Canada / Gouvernement du Canada

MEMORANDUM **NOTE DE SERVICE**

To / À: W. G. Jeffery
MITEC

From / De: Marcia Blanchette
CANMET/MEND

Security Classification – Classification de sécurité
Our File – Notre référence
Your File – Votre référence
Date: 7 April 1992

Subject / Objet

RE: Trip Report - Noranda Technology Centre, April 6, 1992

On April 6, 1992, I travelled by train to meet with Dr E. Yanful, chairman of the MEND Prediction committee, at the Noranda Technology Centre near Montreal.

Briefing of Selected Active Projects:

The remaining funding required for the Mine Doyon Phase II project is $150k over 2 years. The Environmental Innovation Program (EIP) under the Green Plan is being considered as a means of raising this final third. One of the criteria of the program is partial sponsorship by a federal department.

Funding arrangements have been made for the Application of the Ansto Model at Heath Steele (identified as an approved but unfunded project on March 24, 1992), contracts are being finalized.

Discussions on the scope of the third and final year in the Cinola Gold project must be held. The progress report for year two was recently received and is presently being reviewed.

α-evaluation of the ARD database, DBARD is presently being carried out by the BC Task Force Prediction committee, and a ß-evaluation is scheduled for this summer.

Other Issues of Interest:

There are a number of projects which have been initiated by DIAND and are nearing completion. A workshop will be given in Yellowknife on April 28, addressing sampling and chemical prediction techniques directly applicable to the north. An inventory of ARD sites in the territories is nearing completion. This inventory includes kinetic and static prediction data, and I have suggested that the final report include the recommendation that these data be entered into the ARD Database. As well, the cost analysis spreadsheet developed by SRK, for the decommissioning of a site, has been applied to Echo Bay. A reclamation plan has already been done for this site and a comparison of the results will aid in assessing the limitations and advantages of the spreadsheet. Application to other sites may then be considered.

Interest in the use of a "chaotic" approach to modelling has been expressed by B. Godin of the BC Task Force. He has made some contacts, information has been forthcoming, and will be reviewed by the committee.

The Board of Directors Meeting - Decisions and Ramification:
With the approval in principal of the Priority I and II work outlined in the New Plan, the 1992/93 program is required in more detail. Assignments and options were discussed.

The approval of a solicited versus unsolicited future program was also considered, as it affected the committee. The issues to be raised at the April 14 meeting of the secretariat and chairmen were discussed in detail.

Agenda for June 15-19, 1992 in British Columbia
B.C.'s Sixteenth Annual Mine Reclamation Symposium is being held in Smithers, June 16-18. Tours of Bell and Equity Silver are scheduled for the first day.

The next Prediction committee meeting has been scheduled for June 19, in Vancouver. A draft agenda was finalized and notification will be sent out in the future to both members and the contractors that are being asked to make presentations on their work to date.

Monitoring Issues
The draft Waste Rock Sampling Manual which was contracted to SENES was delivered to the Secretariat April 3, and a copy was brought to R. Prairie (of NTC) for his comments. The applicability of sediment sampling to ARD was also discussed. Two firms have forwarded information on their expertise in this area. The differentiation between sediment and sediment porewater is an important one, and one that was not clearly addressed. The relevant information will be circulated to the committee and discussed on May 5, in Ottawa.

cc. Grant Feasby
Manager/MEND Secretariat